Polarity and Acidity of Solvents. Part 3.[1] Polarity of Non-aromatic Polychloro-substituted Solvents

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The empirical solvent polarity parameters $E_T(30)$, (π^*), and (G) have been measured for thirty-four non-aromatic polychloro-substituted solvents. The $E_T(30)$ values of these polychloro-substituted solvents, determined by means of the betaine dyes (**1a**) and (**1b**), are practically insensitive to the solvent polarizability, as previously found for the corresponding $E_T(30)$ values of hydrocarbon and aromatic solvents. The difference between the empirical solvent parameters $E_T(30)$, (π^*), (G), and $\mathcal{S}$* for these three groups of solvents (*i.e.* alkanes, polychloroalkanes, and aromatics) stems above all from their different susceptibility to solvent polarizability. For those polychloroalkanes capable of solute···H–C hydrogen bonding, the empirical solvent parameters depend also on their different sensitivity to the C–H acidity of the solvent.

Physical properties of molecules and their chemical reactivities in solution are usually strongly influenced by the polarity of the surrounding solvent molecules. Solvent polarity in this respect is determined by the general solvation capability of the solvent which in turn depends on the action of all possible intermolecular forces, both specific and non-specific, between solute and solvent molecules.[2] There have been several attempts to correlate solvent-dependent molecular properties and reactivities with so-called empirical parameters of solvent polarity derived from other solvent-dependent reference processes such as u.v./visible absorptions [*e.g.* $E_T(30)$,[3] π^*[4]], i.r. absorptions (*e.g.* G [5]), or chemical reactivities (*e.g.* $\mathcal{S}$ [6,7]).

We have already shown[1] that for the group of aromatic solvents these empirical solvent polarity parameters differ mainly in the variable contribution of the polarizability term to the overall solute/solvent interaction, as measured classically by the function $f(n) = (n^2 - 1)/(2n^2 + 1)$ of the solvent refractive index, n. Likewise, we have shown[8] that for the solvent group of alkanes, cycloalkanes, and tetraalkylsilanes the empirical parameter $E_T(30)$ depends only to a minor extent on $f(n)$ (correlation coefficient $r = 0.29$ for eleven solvents), in contrast to the empirical parameter π^* which is more strongly correlated with $f(n)$ ($r = 0.992$ for eight solvents).

Another group of solvents, equally important for industrial and laboratory applications, consists of non-aromatic polychlorosubstituted alkanes, alkenes, and cycloalkanes such as dichloromethane, chloroform, tetrachloromethane, trichloroethene, and chlorofluoroalkanes (*e.g.* Freons, Genetrons, and Frigens). In the present work we determine the empirical parameters $E_T(30)$,[3] (π^*),[4] and (G)[5] for thirty-four polychloro-substituted solvents, and we then investigate these parameters by means of correlation equation (1), with the

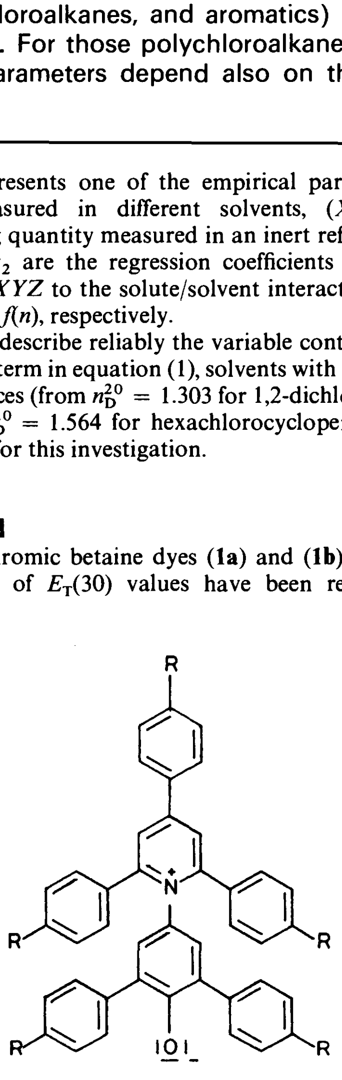
$$XYZ = (XYZ)_0 + a_1 \cdot E_T(30) + a_2 \cdot f(n) \qquad (1)$$

inclusion of the empirical parameter $\mathcal{S}$[6,7] which is already known for thirteen polychloro-substituted solvents. In equation (1), XYZ represents one of the empirical parameters under question measured in different solvents, $(XYZ)_0$ is the corresponding quantity measured in an inert reference solvent, and a_1 and a_2 are the regression coefficients describing the sensitivity of XYZ to the solute/solvent interactions measured by $E_T(30)$ and $f(n)$, respectively.

In order to describe reliably the variable contribution of the polarizability term in equation (1), solvents with a wide range of refractive indices (from $n_D^{20} = 1.303$ for 1,2-dichlorohexafluoropropane to $n_D^{20} = 1.564$ for hexachlorocyclopentadiene) have been selected for this investigation.

Experimental

The solvatochromic betaine dyes (**1a**) and (**1b**)† used for the determination of $E_T(30)$ values have been reported in the literature.[3b,9a,b] The u.v./visible spectra of the betaine dyes and of 4-nitroanisole at 25 °C, as well as the i.r. spectra of acetophenone at 21 °C, were recorded as previously described.[1,8,10] Immediately before use, the solvents were



(**1a**) R = H

(**1b**) R = Bu^t

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* $\mathcal{S} = \log k_2\{[\mathrm{Pr_3N}] + [\mathrm{MeI}]\}$.

† In Part 1 of this series[8] the formulae numbers corresponding to (**1a**) and (**1b**) in this paper are (**1a**) (**1d**), respectively.

distilled and dried over molecular sieves (4 Å) then percolated through a chromatography column filled with basic aluminium oxide (activity I). Purity was checked by gas chromatography with Carbowax and Apiezon columns. The water content (generally less than 100 ppm) was determined gas chromatographically by means of a Porapak Q column. In order to exclude moisture from the dye solutions, the preparation was carried out in a glove box under dry air.

However, the visible absorption spectrum of betaine dye (**1b**) in 1,1,1-trichloroacetone as solvent is abnormally sensitive to small amounts of water. The position of the long-wavelength solvatochromic absorption band is $\lambda_{max.} = 605$ nm for a dye solution containing 130 ppm of water, and $\lambda_{max.} = 635$ nm for a dye solution containing 30 ppm of water. It is well known that the extent of hydration of ketones is very large when electron-withdrawing substituents, such as CCl_3, are present. Therefore, the hypsochromic shift of the solvatochromic band of (**1b**) with increasing water content must be attributed to a small amount of the hydrate $CCl_3C(OH)_2CH_3$, the concentration of which is not negligible when compared with the concentration of the betaine dye in 1,1,1-trichloroacetone (*ca.* 10^{-4} mol dm^{-3}). The $E_T(30)$ value for 1,1,1-trichloroacetone, given in the Table (No. 22), corresponds to a solvent which contains a small amount of the corresponding hydrate due to non-removable traces of water (*ca.* 30 ppm) and should be considered as a tentative value.

Results

The empirical parameters of solvent polarity, determined in this work for non-aromatic polychloro-substituted alkanes, alkenes, and cycloalkanes, are given in the Table. Also presented in the Table are the following solvent parameters.

(*a*) The Dimroth–Reichardt parameter $E_T(30)$, derived from the wavelength λ_1 of the long-wavelength intramolecular charge-transfer absorption band of the standard betaine dye (**1a**) from equation (2),[3,8] and from the corresponding wavelength λ_2 of the more lipophilic secondary standard betaine dye (**1b**) from equation (3).[8] For reasons already

$$E_T(30) = \frac{hcN_A}{\lambda_1} = \frac{28591}{\lambda_1} \qquad (2)$$

$$E_T(30) = \left(\frac{28591}{\lambda_2} - 1.808\right)\frac{1}{0.9424} \qquad (3)$$

$E_T(30)$ in kcal mol^{-1}; λ_1 and λ_2 in nm

given, the $E_T(30)$ value of 1,1,1-trichloroacetone is, at 45.9 kcal mol^{-1}, rather high compared with the $E_T(30)$ values of related solvents such as acetone (42.2) and methyl trichloroacetate (39.6), in spite of the fact that the corresponding dielectric constants are in the same range for all three solvents (ε_r = 10.4, 20.9, and 8.8, respectively). Therefore, the high $E_T(30)$ value of 1,1,1-trichloroacetone, revealing the presence of traces of the hydrate, is not included in the following correlations.

(*b*) The wavenumber in kilokayser (1 kK = 10^3 cm^{-1}) of the long-wavelength π–π^* absorption band of 4-nitroanisole, designated as (π^*). This quantity (π^*) is related to the π^* parameter introduced by Taft *et al.*[4]

(*c*) The wavenumber, in cm^{-1}, of the i.r. stretching vibration of the carbonyl group in acetophenone, designated (G) in this paper. This quantity (G) is related to the G-values of Allerhand and Schleyer.[5]

(*d*) The $\mathscr{S}$-parameter of Drougard and Decroocq,[6,7] which is equal to the values of log k_2 for the S_N2 Menschutkin reaction between tripropylamine and iodomethane at 20 °C, according to the Scheme.

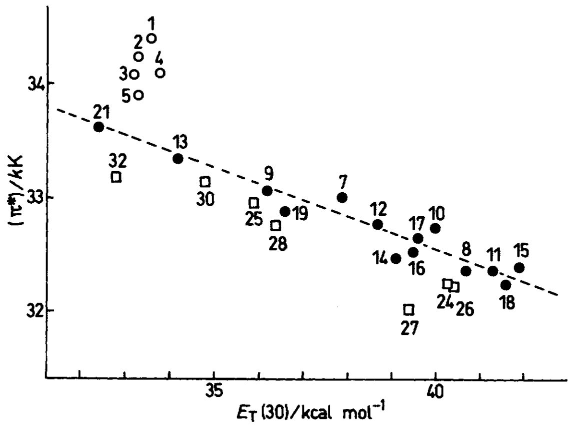
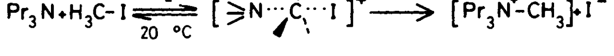


Figure. Correlation between (π^*) and $E_T(30)$ values for 26 solvents of different refractive index. ○ $n < 1.40$; ● $1.40 < n < 1.47$; □ $1.47 < n$. Numbering of solvents as in Table.



Scheme.

Discussion

(A) *Comparison of the Solvent Parameters* $E_T(30)$ *and* (π^*).—Although Taft *et al.*[11] have found a correlation coefficient of $r = 0.995$ for six polychloro-substituted solvents, the correlation coefficient for the linear correlation between $E_T(30)$ and (π^*) for 26 polychloro-substituted solvents of our choice is in fact only equal to 0.880 (see the Figure). Solvents with refractive indices between 1.40 and 1.47 are distributed close to the straight correlation line, whereas solvents with refractive indices < 1.40 are found above the line, and solvents with $n > 1.47$ are found below this line. Obviously, a polarizability term must be added to the $E_T(30)$/(π^*) correlation. Indeed, the correlation between $E_T(30)$ and (π^*) for the same 26 polychloro-substituted solvents can be greatly improved by application of equation (4)

$$(\pi^*) = 42.4 - [0.1563\, E_T(30)] - [17.4 f(n)] \qquad (4)$$

to this correlation ($r = 0.985$). This equation reveals a greater influence of solvent polarizability on the π–π^* absorption of 4-nitroanisole than on the charge-transfer absorption of the betaine dye. For this reason, the correlation coefficient for the correlation between (π^*) and $f(n)$ is significant with $r = 0.714$ for the 26 polychloro-substituted solvents, whereas no significant correlation exists between $E_T(30)$ and $f(n)$ as shown by the correlation coefficient of $r = 0.337$ for the same 26 solvents. If two additional solvents with particularly high refractive indices are added to this correlation (*e.g.* hexachlorobutadiene and hexachlorocyclopentadiene), the correlation coefficient drops further to $r = 0.104$.

These observations are in agreement with the results of the $E_T(30)$/(π^*) correlations obtained for alkanes[8] and aromatics[1] as solvents. Accordingly, it can be stated that the $E_T(30)$ parameter in effect does not measure the polarizability effects (*i.e.* non-specific dispersion and inductive forces) of the solvents. The dispersion interaction between betaine dipoles and solvent molecules, which leads to a bathochromic shift of the betaine absorption band, is compensated by the inductive solute/solvent

Table. Refractive index, n_D^{20}, its function $f(n) = (n^2 - 1)/(2n^2 + 1)$, and the empirical solvent polarity parameters $E_T(30)$, (π^*), (G), and $\mathcal{S}$ for 34 polychlorosubstituted solvents.

Number	Solvent	n_D^{20} [a]	$f(n)$	$E_T(30)$/ kcal mol^{-1} [b]	(π^*) [c]	(G) [d]	$\mathcal{S}$ [e]
1	1,2-Dichlorohexafluoropropane	1.303	0.159	33.6	34.40	1 696.2	
2	1,2-Dichlorohexafluorocyclobutane	1.333	0.171	33.3	34.24	1 696.0	
3	1,1,2-Trichlorotrifluoroethane	1.358	0.180	33.2	34.08	1 694.1	
4	1,1,1-Trichlorotrifluoroethane	1.360	0.181	33.8	34.09	1 693.4	
5	Trichlorofluoromethane (at 20 °C)	1.383	0.189	33.3	33.89	1 693.1	
6	Trichloromethylsilane	1.412	0.199	*f*	33.28	1 690.8	
7	2,2-Dichloropropane	1.415	0.200	37.9	33.01	1 689.6	
8	Dichloromethane	1.424	0.203	40.7	32.36	1 684.4	2.447
9	1,1,1-Trichloroethane	1.438	0.208	36.2	33.07	1 689.7	
10	Trichloroacetonitrile	1.440	0.209	40.0	32.74	1 687.0	
11	1,2-Dichloroethane	1.445	0.210	41.3	32.37	1 685.2	2.580
12	Ethyl trichloroacetate	1.450	0.212	38.7	32.78	1 688.1	1.602
13	(*E*)-1,2-Dichloroethene	1.446	0.211	34.2	33.34	1 689.0	0.699
14	Trichloromethane, chloroform	1.446	0.211	39.1	32.47	1 682.8	2.11
15	(*Z*)-1,2-Dichloroethene	1.449	0.211	41.9	32.40	1 685.1	2.146
16	1,4-Dichlorobutane	1.454	0.213	39.5	32.53	1 686.4	2.279
17	Methyl trichloroacetate	1.454	0.214	39.6	32.65	1 687.3	
18	Bis(2-chloroethyl) ether	1.457	0.214	41.6	32.25	1 684.9	
19	1,10-Dichlorodecane	1.460	0.215	36.6	32.88	1 688.7	
20	Phosphorus oxychloride	1.460	0.215	*f*	32.43	1 687.0	
21	Tetrachloromethane	1.461	0.215	32.4	33.62	1 691.0	0.15
22	1,1,1-Trichloroacetone	1.462	0.216	45.9	32.61	1 687.1	
23	4,5-Dichloro-1,3-dioxolan-2-one	1.463	0.216	*f*	31.91	1 681.3	
24	1,1,2-Trichloroethane	1.471	0.218	40.3	32.25	1 683.7	2.519
25	Trichloroethene	1.476	0.220	35.9	32.96	1 688.0	0.964
26	1,2,3-Trichloropropane	1.484	0.222	40.4	32.24	1 684.2	
27	1,1,2,2-Tetrachloroethane	1.494	0.225	39.4	32.02	1 682.0	2.940
28	Pentachloroethane	1.503	0.228	36.4	32.76	1 684.9	1.519
29	Tetrachloroethene	1.505	0.229	*g*	33.52	1 691.8	−0.22
30	Bromotrichloromethane	1.505	0.229	34.8	33.14	1 687.1	
31	Hexachloroacetone	1.511	0.231	*f*	32.94	1 687.8	
32	Hexachloropropene	1.550	0.242	32.8	33.18	1 689.9	
33	Hexachlorobutadiene	1.556	0.243	32.2	*h*	1 691.3	
34	Hexachlorocyclopentadiene	1.564	0.245	32.8	*h*	1 690.7	

[a] Measured with an Abbe refractometer. [b] This work. Measured with betaine dyes (**1a**) and (**1b**). [c] This work. Measured with 4-nitroanisole. [d] This work. Measured with acetophenone. [e] Values from ref. 6. [f] No value because of chemical reaction between solvent and betaine dye. [g] No value since the maximum of the long-wavelength solvatochromic betaine absorption band is too close to the limit of our spectrophotometer (900 nm) to be measured with precision. [h] Non-measurable even with a cell of only 30 μm thickness because of solvent absorption.

interactions, which for their part lead to a hypsochromic band shift in the case of highly dipolar betaine molecules. However, the dispersion interaction, which always leads to a bathochromic band shift whatever the electronic transition is, and the inductive interaction between the less dipolar 4-nitroanisole and solvent molecules, act additively to bring about a bathochromic shift for the $\pi \longrightarrow \pi^*$ absorption of 4-nitroanisole.

Other attempts to improve the correlation between $E_T(30)$ and π^* using modified parameters of Taft *et al.* (*e.g.* π_n^*) are described in refs. 12 and 13.

(B) *Comparison of the Solvent Parameters* $E_T(30)$ and (G).—The correlation coefficient between the u.v./visible spectroscopic parameter $E_T(30)$ and the i.r. spectroscopic parameter (G) for 28 polychlorosubstituted solvents is only 0.806. It is entirely possible that the reason for this less than satisfactory linear correlation between the two solvent parameters arises again from different contributions of the polarizability term to the solute/solvent interaction, in so far as, for the same 28 solvents, $E_T(30)$ correlates poorly with $f(n)$ ($r = 0.337$), whereas (G) correlates much better with $f(n)$ ($r = 0.733$). Therefore, it is not surprising that the correlation coefficient rises to $r = 0.931$ for the two-parameter equation (5), calculated

$$(G) = 1\,740.1 - [0.89\,E_T(30)] - [90 f(n)] \qquad (5)$$

for the same 28 polychloro-substituted solvents. There are, however, systematic deviations below the straight correlation line defined by equation (5) for the following solvents:

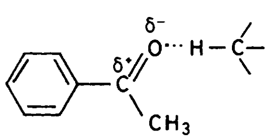
$$CHCl_3\,(-3.5) < Cl_2HCCHCl_2\,(-2.8) < Cl_2HCCCl_3\,(-2.3) < (E)\text{-}ClHC{=}CHCl\,(-1.7) < BrCCl_3\,(-1.4) < CH_2Cl_2\,(-1.2) < Cl_2HCCH_2Cl\,(-0.9)$$

The deviations in cm^{-1} are given in parentheses and should be considered with respect to the precision with which the (G)-values were determined (*ca.* 0.2 cm^{-1}).

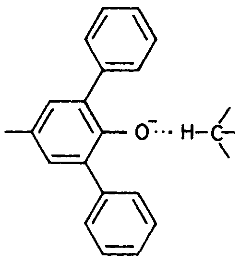
All solvents which deviate are either C–H hydrogen-bond donors, as known from spectroscopic and thermodynamic investigations,[14,15] or C–Hal halogen-bond donors[16] exemplified by Cl_3C–Br, in which the electron-accepting character of the bromine atom is of similar type as in F_3C–Br[17] and F_3C–I.[18] For polychloroalkanes, the hydrogen-bond donating capability increases with the number of chlorine atoms per carbon atom and reaches a maximum with chloroform. The hydrogen-bond donating capability also increases with the number of hydrogen atoms carrying a positive charge ($C^{\delta-}$–$H^{\delta+}$). Thus, Cl_3CCHCl_2 with 5Cl:2C, and only one positively charged hydrogen atom, deviates less than $Cl_2HCCHCl_2$ with 4Cl:2C and two positively charged hydrogen atoms.

Of the polychloroalkenes, (*E*)-1,2-dichloroethene is the only solvent that deviates clearly from the linear correlation line defined by equation (5). Neither (*Z*)-1,2-dichloroethene nor trichloroethene deviate significantly. The smaller hydrogen-bond donating capability of the *Z*-isomer with respect to its *E*-counterpart is well documented.[14] The unexpected behaviour of trichloroethene, however, needs further confirmation and analysis.

The deviation of these electron-accepting solvents from the correlation line given by equation (5) can be best explained by the different susceptibility of (*i*) the C=O stretching vibration of acetophenone, and (*ii*) the charge-transfer absorption of the betaine dyes, to C–H hydrogen-bonding interactions (and C–Hal halogen-bonding interactions) as indicated by (**2**) and (**3**). If the seven polychloro-substituted solvents capable of specific solute/solvent interactions are excluded, the single-parameter correlation between $E_T(30)$ and (*G*) for 28 − 7 = 21 solvents is clearly improved (r = 0.856 instead of 0.806). The correlation coefficient of the two-parameter equation (5) increases from r = 0.931 to r = 0.989 if applied to the same set of 21 solvents.



(**2**)



(**3**)

(C) *Comparison of the Solvent Parameters* $E_T(30)$ *and* $\mathscr{S}$.—There is a fair correlation between $E_T(30)$ and $\mathscr{S}$ for 12 polychloro-substituted solvents (r = 0.913). It is slightly improved with the inclusion of function $f(n)$ to give a two-parameter equation with r = 0.938. However, this improvement is not very significant because $\mathscr{S}$ is available from the literature[6,7] for only 12 polychloro-substituted solvents, with a rather small variation in $f(n)$ from 0.202 to 0.228.

Interestingly, there exists a rather good correlation between $\mathscr{S}$ and (π^*); r = 0.982 for 13 polychloro-substituted solvents. The various solute/solvent interactions of polychloro-substituted solvents (*i.e.* dipolarity, polarizability, H-bonding) seem to exert a similar influence on the second-order rate constant of the S_N2 reaction (Scheme), and the $\pi \longrightarrow \pi^*$ absorption of 4-nitroanisole. It should be remembered that we have already found a good correlation between $\mathscr{S}$ and (π^*) for 12 aromatic solvents (r = 0.973).[1]

Conclusions

Non-specific solute/solvent interactions for the non-aromatic, polychloro-substituted solvents shown in the Table can indeed by described by means of the simple two-parameter equation (1). The regression coefficients a_1 and a_2 measure reliably the different susceptibility of the solvent-dependent property *XYZ* to (i) solvation effects as determined by $E_T(30)$ (*i.e.* solvent dipolarity and acidity), and (ii) solvent polarizability, because the vectors $E_T(30)$ and $f(n) = (n^2 - 1)/(2n^2 + 1)$ are nearly orthogonol to each other for the polychloro-substituted solvents in the Table. However, for solvent-dependent properties *XYZ* which are different functions of (*i*) the H-bond acidity of the solvent and (*ii*) the $E_T(30)$ parameter, a C–H bond (and C–Hal bond) acidity term has to be added to equation (1) for those polychloro-substituted solvents in the Table that are hydrogen-bond donors (*e.g.* Cl_3C–H) or halogen-bond donors (*e.g.* Cl_3C–Br).

Together with the new $E_T(30)$ values in the Table, the empirical solvent polarity parameter $E_T(30)$, now known for more than 300 solvents,[1–3,8] constitutes one of the most comprehensive solvent polarity scales. After the investigation of alkanes and cycloalkanes,[8] aromatic solvents,[1] and non-aromatic polychlorosubstituted alkanes, alkenes, and cycloalkanes (this work), a subsequent paper will deal with aliphatic solvents that contain one functional group such as RCN, RNO_2, $R_2C{=}O$, and R_2O. This will then permit a comparison of the solvent polarity parameters for all four classes of solvents.

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